Frequency Dependence and Anisotropy of the Glass Transition T_g of $Rb_{0.52}(ND_4)_{0.48}D_2PO_4$

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FREQUENCY DEPENDENCE AND ANISOTROPY OF THE GLASS TRANSITION T_g OF $Rb_{0.52}(ND_4)_{0.48}D_2PO_4$

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Abstract The frequency dependence of the glass transition temperature T_g has been calculed from the Vogel-Fulcher law using dielectric data obtained in the 10^2 Hz to 10^{10}Hz region. The best fit was obtained with $\ln f_o = 29$ and $T_o = 38$ K. The anisotropy of T_g predicted recently by theory has been observed.

EXPERIMENTAL RESULTS AND DISCUSION

Studies of the frequency-dependent dielectric properties of $Rb_{0.52}(ND_4)_{0.48}D_2PO_4$ at low frequency were done by Samara and Schmidt[1] and others[2,3]. In this paper we report the real ε' and imaginary ε'' dielectric permittivity in the X-band microwave region for temperatures from 5 K to 180 K. Typical rounded cusp dependence for $\varepsilon'(T)$ and narrow rounded maximum for $\varepsilon''(T)$ were observed.Treating this maximum as the temperature T_g of the glass "transition", T_g=86 K for f=9.3 GHz when the microwave electric field is parallel to the c-axis of the $Rb_{0.52}(ND_4)_{0.48}D_2PO_4$ mixed crystal (FIGURE 1).

According to cluster models of proton glass[4] , short range interactions form partly ordered clusters imbedded in the frustrated proton system. The clusters have a mean relaxation time τ strongly related to their volume and temperature, and τ decreases rapidly with increasing temperature. According to another viewpoint, to be explained in detail elsewhere[5], the τ distribution is governed by effective diffusion of HPO_4 and H_3PO_4 defects. In either case, the

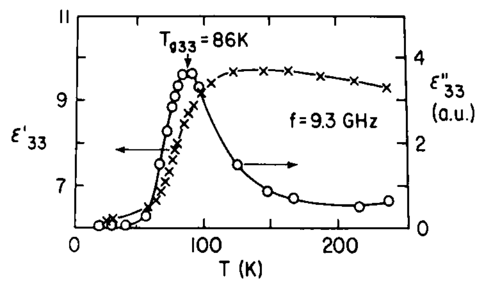

FIGURE 1 Temperature dependences of the real ε'_{33} and imaginary ε''_{33} parts of dielectric permittivity of 72% deuterated RADP.

mean τ is given by the Vogel-Fulcher law[6] :

$$\tau^{-1}=f_0\exp(-E/k(T-T_0)), \qquad (1)$$

where f_0 and T_0 are scaling parameters and E is an activation energy. The frequency f_0 is the O-D...O deuteron intrabond transfer attempt frequency, and T_0 should be treated as the temperature below which the O-D...O deuteron system is "frozen". Courtens[2] proposed that Eq.(1) should be modified to the form:

$$\tau^{-1}=f_0\exp(-E/k(T-T_0)^{\alpha}) \; . \qquad (2)$$

At the temperature giving maximum ε'' we can say that $\tau^{-1}=f$, where f is the measurement frequency and $T=T_g$. Then Eq.(2) gives the formula :

$$(\ln f_0-\ln f)^{-1}= k(T_g-T_0)^{\alpha}/E \; . \qquad (3)$$

Figure 2 shows the plot of Eq.(2) for $\alpha=2$, $\ln f_0=29$ and $T_0=38$ K, using our experimental point and low frequency measurements[1,3] for ε''_{33} . The good agreement shows that the Eq.(2) form of the Vogel-Fulcher law describes the proton glass system in our crystal. The values of $\ln f_0$ and T_0 are practically the same as found by Courtens[2], $\ln f_0=28.5$ and $T_0=30$ K for $Rb_{0.38}(ND_4)_{0.62}D_2PO_4$. In terms of physical parameters, these results illustrate the rapid slowing down of dynamic processes with decreasing temperature, and depending on the model adopted, the increase in cluster size[4] or the increase in defect diffusion path length between creatio and annihilation[5].

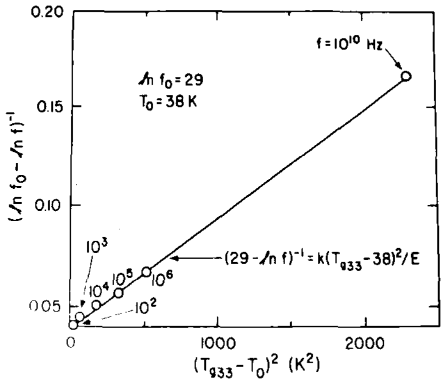

FIGURE 2 A plot of $(\ln f_0-\ln f)^{-1}$ vs. $(T_{g33}-T_0)^2$ for $\ln f_0=29$ $T_0=38$ K and $\alpha=2$.

Matsushita and Matsubara[7] (MM) using a cluster theory[4] predicted anisotropy of T_g- different values of T_g for susceptibility along the c and a axes. They introduced two order parameters, q_x and q_z, which give the temperatures T_{g11} and T_{g33}. Figure 3 shows that for $Rb_{0.52}(ND_4)_{0.48}D_2PO_4$ the ε'' maxima occur at different temperatures for microwave electric field parallel to the a and c axes. Our data show $T_{g11}=82$ K and $T_{g33}=86$ K, in accord with MM theory which gives $T_{g33}>T_{g11}$ for concentration $x<0.5$. Further experiments are planned.

CONCLUSION

These experiments show that dielectric behavior for proton glasses obeys the Vogel-Fulcher law also when these is isotropic randomness (72 % deuteration) as well as cation randomness (48 % ND_4). In addition, the anisotropy of T_g predicted by Matsushita and Matsubara [7] was observed.

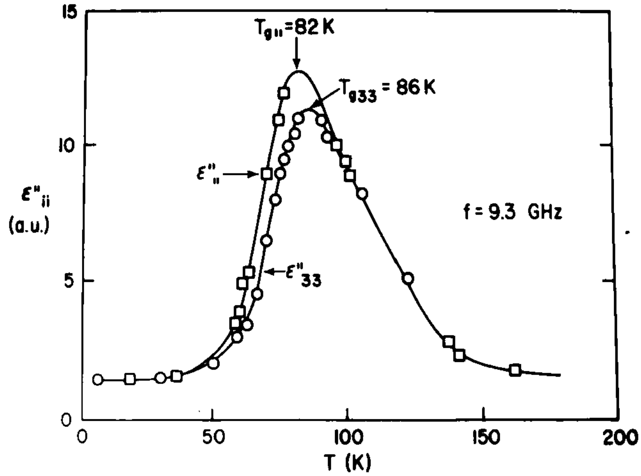

FIGURE 3 Temperature dependences of the imaginary part of electric permittivity in arbitrary units for two orientations of microwave electric field: ε''_{33} and ε''_{11} .

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